



Challenge

Measuring the AOX content properly in the presence of more than $> 1\text{g/L}$ inorganic bound Cl.

Solution

Using the smart solid phase extraction autosampler APU 28 SPE offers a fast, effortless, and fully automated SPE-AOX sample preparation.

Determination of Adsorbable Organic Halogens in Highly Saline Water Samples after Solid Phase Extraction (SPE-AOX)

Introduction

An easy and fully automated method for the correct determination of AOX contents in the presence of extremely high ($c > 1\text{ g/L}$) quantities of inorganic halides is often needed when analyzing marine water samples, industrial wastewater and brine applications (SPE-AOX according to ISO 9562:2004). The presence of high amounts of inorganic halogen compounds negatively affects the determination of AOX. When such samples are analyzed directly by means of common AOX methods (adsorption on charcoal and combustion), results will be falsified and too high. To avoid this, the interfering compounds have to be removed before the adsorption. Solid phase extraction (SPE) has proven to be the most efficient and easy method to do this.

For the measurement, the samples were enriched on SPE cartridges. To achieve an easy and effective segregation between organic and inorganic matter, a polymer resin was used for separation. The resin captures only the organic halogen compounds, while letting the inorganic material pass through. The AOX was then eluted with methanol and diluted in ultrapure water. This mixture was adsorbed on prefilled charcoal columns, followed by a final washing process to ensure a complete separation of inorganic and organic halogen compounds.

Since this is a time-consuming process, laboratories facing increasing time and work pressure strive to facilitate the workflow. The sample preparation unit APU 28 SPE enables fast and unattended, fully automated preparation of SPE-AOX samples, thus highly shortening processing time. Combined with the multi X 2500 AOX analyzer, the APU 28 SPE ensures fast, precise and reliable results, which are mandatory for laboratories.

Materials and Methods

Samples and Reagents

- Water samples with high load of inorganic chlorides (> 1 g/L)
- Standard solution: 100 µg/L p-chlorophenol
- NaNO₃ washing solution
- 0.01 M HCl

As micro coulometric Cl determination is an absolute method, no calibration was needed.

Instrumentation

The samples were prepared automatically using an APU 28 SPE system. For the combustion of samples, a multi X 2500 analyzer in vertical operation mode with AOX combustion tube and the standard sensitive cell was used. Sample introduction was carried out fully automated by means of the autoX 36 autosampler.

Method parameters

Standard method settings from the method library were applied. The parameter settings for the combustion process and the sample transfer are summarized in table 1. The evaluation parameters for the detection of chlorine are given in table 2.

Table 1: Settings for sample preparation (ISO 9562:2004)

Parameter APU 28 SPE Sample Preparation	Specification
Sample volume (SPE cartridge)	100 mL
Sample volume (AOX column)	100 mL
Washing volume (SPE and AOX step)	25 mL
Methanol volume (conditioning)	10 mL
Methanol volume (elution)	5 mL
Adsorption speed	3 mL/min

Table 2: Settings for AOX determination (acc. ISO 9562:2004)

Parameter multi X 2500 AOX determination	Specification
Furnace temperature	> 950 °C
Titration delay	approx. 240 s
Max. titration time	1200 s
Cell temperature	18–35 °C
Quality oxidation/carrier gas	Oxygen 4.5
Working range coulometric cell (AOX)	1 µg–100 µg Cl abs.
Working range chlorine module	10 ng–1000 µg Cl abs.
Automation	autoX 36 or autoX 112

Results and Discussion

The column method was used according to ISO 9562:2004. Before being enriched on activated carbon, the sample underwent an SPE process to separate inorganic from organic bound halides (Figure 1). Figure 2 shows the APU 28 SPE during the automatic elution of the SPE cartridges with methanol. The SPE procedure, which works without any manual intervention, and the adsorption step itself were performed automatically by the APU 28 SPE sample preparation unit.

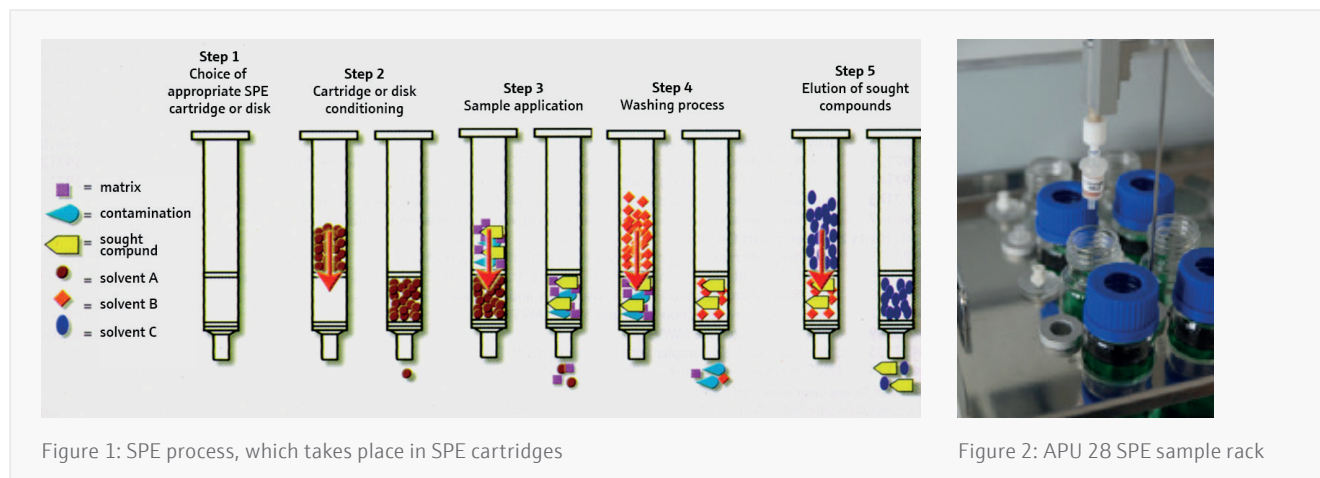


Figure 1: SPE process, which takes place in SPE cartridges

Figure 2: APU 28 SPE sample rack

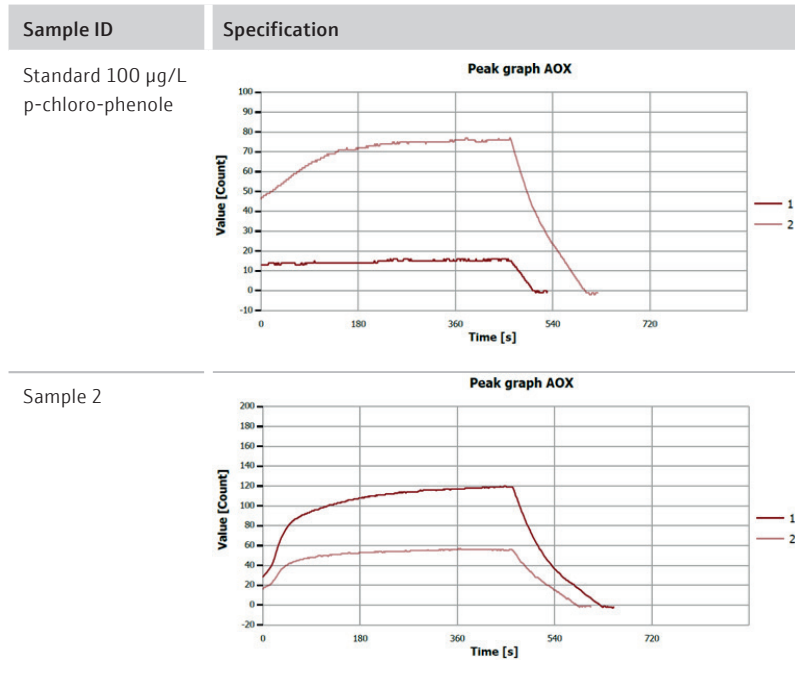
The treated water samples ran through two adsorption columns (prefilled charcoal containers) with a flow rate of 3 mL/min. The charcoal-filled containers were then rinsed with 25 mL of nitrate washing solution to remove the inorganic salt load at the same flow rate.

The prepared charcoal containers were placed into the autoX 36's sample plate. This sampling system automatically introduces the loaded columns into the vertically arranged open AOX combustion tube. The furnace temperature of 950 degrees Celsius was chosen in compliance with DIN EN ISO 9562:2004. The organic halogen compounds were converted in the presence of a surplus of oxygen to HCl gas. After sufficient drying with concentrated sulphuric acid, the HCl gas was transferred into the sensitive cell. The cell has a wide working range from 1 µg to 100 µg chlorine absolute. The chlorine detection was carried out by means of microcoulometric titration. Proper operation of the analysis system was confirmed by analysis of a commercial standard solution (4-chloro-phenole in water).

Table 3: Settings for AOX determination (acc. ISO 9562:2004)

Sample ID	Adsorption Volume [mL]	Dilution ratio	abs. Cl value Column 1 [µg]	abs. Cl value Column 2 [µg]	Blank value [µg abs.]	Result [µg/L]
Standard	100	1:1	10.5	0.23	0.3	104.3
1	100	50:100	1.51	0.18	0.3	27.8
2	100	20:100	2.67	0.62	0.3	149.5
3	50	50:100	0.64	0.51	0.3	34.0
Standard	100	1:1	9.67	0.52	0.3	9.89

Table 4: Signal profile of a para-chloro-phenole standard solution and of sample 2



Conclusion

The APU 28 SPE system is fully suited for the automatic preparation of AOX and SPE-AOX samples. Due to its workflow automation, including all adsorption and rinsing steps, the APU 28 SPE is an ideal partner for high sample throughput. In combination with its continuous flow principle, a fast, efficient and accurate analysis is achieved. The multi X 2500 is an excellent instrument for AOX (EOX, POX, and TX/TOX) determination in all kinds of water, sludge, and soil samples, as well as other organic liquids and solids (e.g., used oil). Due to its enormous flexibility, changing between different parameters is fast and easy. This makes the multi X 2500 very efficient, saving valuable time and costs.

References

¹⁾ DIN EN ISO 9562 – Water quality - Determination of adsorbable organically bound halogens (AOX) (ISO 9562:2004); German version EN ISO 9562:2004

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